

FORM PTO-1390  
(REV. 9-2001)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

Mo-6712/LeA 34,285

U.S. APPLICATION NO. (If known, see 37 CFR 1.5

10/019996  
To be Assigned

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP00/03493

18 April 2000 (18.04.00)

25 April 1999 (25.04.99)

TITLE OF INVENTION

METHOD FOR THE DIHYDROXYLATION OF OLEFINS USING TRANSITION-METAL CATALYSTS

APPLICANT(S) FOR DO/EO/US 1) Matthias Beller; 2) Christian Dobler; 3) Gerald Mehlretter; 4) Uta Sundermeier

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☒ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Preliminary Amendment w/Abstract; Copy of IB/306 (2)

10/019996  
U.S. APPLICATION NO. (If known, see 37 CFR 1.53)  
To be Assigned

INTERNATIONAL APPLICATION NO.  
PCT/EP00/03493

531 Rec'd PCT/PTC 19 OCT 2007  
ATTORNEY'S DOCKET NUMBER  
Mo-6712/LeA 34,285

21. ☒ The following fees are submitted:

**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482)  
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO  
and International Search Report not prepared by the EPO or JPO. . . . . \$1040.00

International preliminary examination fee (37 CFR 1.482) not paid to  
USPTO but International Search Report prepared by the EPO or JPO . . . . . \$890.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO  
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . \$740.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . \$100.00

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

**CALCULATIONS PTO USE ONLY**

\$ 890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	16 - 20 =	0	x \$18.00

\$

Independent claims	1 - 3 =	0	x \$84.00
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\$

MULTIPLE DEPENDENT CLAIM(S) (if applicable)	+ \$280.00
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\$ 0.00

**TOTAL OF ABOVE CALCULATIONS =**

\$ 890.00

☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above  
are reduced by 1/2.

\$ 0.00

**SUBTOTAL =**

\$ 890.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

**TOTAL NATIONAL FEE =**

\$ 890.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

\$ 40.00

**TOTAL FEES ENCLOSED =**

\$ 930.00

Amount to be  
refunded: \$

charged: \$

- a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 930.00 to cover the above fees.  
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card  
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



00157

PATENT TRADEMARK OFFICE

Richard E.L. Henderson  
SIGNATURE

Richard E.L. Henderson  
NAME

31,619  
REGISTRATION NUMBER

531 Rec'd PGT

10/019996

19 OCT 2001

PATENT APPLICATION

Mo6712

LeA 34,285

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

## APPLICATION OF

MATTHIAS BELLER ET AL

SERIAL NUMBER: TO BE ASSIGNED

FILED:            HEREWITH

TITLE: METHOD FOR THE DIHYDROXYLATION  
OF OLEFINS USING TRANSITION-METAL  
CATALYSTS

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

Prior to examination, please amend the application as follows.

"Express Mail" mailing label number ET671450313US

Date of Deposit October 19, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or letter)

Signature of person mailing paper or fee)

IN THE SPECIFICATION:

Please replace the title at page 1, line 1, with

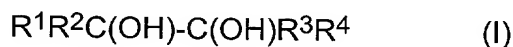
--METHOD FOR THE DIHYDROXYLATION OF  
OLEFINS USING TRANSITION METAL CATALYSTS --

IN THE CLAIMS:

Please replace the heading at page 18, line 1, with --WHAT IS CLAIMED IS:--

Claims 1-12 have been canceled in favor of replacement Claims 13-28.

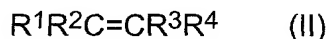
--13. A process for the dihydroxylation of olefins using transition metal catalysts to obtain monofunctional, bifunctional, and/or polyfunctional 1,2-diols of the formula (I)



where

R<sup>1</sup> to R<sup>4</sup> are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, COO-aryl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, O-CO-aryl, O-CO-alkyl, OCOO-alkyl, N-alkyl<sub>2</sub>, NH-alkyl, N-aryl<sub>2</sub>, NH-aryl, NO, NO<sub>2</sub>, NOH, aryl, fluorine, chlorine, bromine, iodine, Si-alkyl<sub>3</sub>, CHO, SO<sub>3</sub>H, SO<sub>3</sub>-alkyl, SO<sub>2</sub>-alkyl, SO-alkyl, CF<sub>3</sub>, NHCO-alkyl, CONH<sub>2</sub>, CONH-alkyl, NHCOH, NHCOO-alkyl, CHCHCO<sub>2</sub>-alkyl, CHCHCO<sub>2</sub>H, PO-(aryl)<sub>2</sub>, PO(alkyl)<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, or PO(O-alkyl)<sub>2</sub>, where alkyl is a linear, branched, and/or cyclic aliphatic organic group having from 1 to 18 carbon atoms and aryl is a 5-, 6-, or 7-membered aromatic ring containing from 4 to 14 carbon atoms and from 0 to 3 heteroatoms and is optionally fused, and where the alkyl and/or the aryl group optionally bears up to six substituents selected independently from the group consisting of hydrogen, alkyl, O-alkyl, OCO-alkyl, O-aryl, aryl, fluorine, chlorine, bromine, iodine, OH, NO<sub>2</sub>, NO, Si-alkyl<sub>3</sub>, CN, COOH, CHO, SO<sub>3</sub>H, NH<sub>2</sub>, NH-alkyl, N-alkyl<sub>2</sub>, PO-alkyl<sub>2</sub>, SO<sub>2</sub>-alkyl, SO-alkyl, CF<sub>3</sub>, NHCO-alkyl, COO-alkyl, CONH<sub>2</sub>, CO-alkyl, NHCOH, NHCOO-alkyl, CO-aryl, COO-aryl, PO-aryl<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, PO(O-alkyl)<sub>2</sub>, and SO<sub>3</sub>-alkyl, where alkyl and aryl are as defined above,

comprising reacting an olefin of the formula (II)



where  $R^1$  to  $R^4$  are defined as for formula (I),  
with molecular oxygen in the presence of an osmium, ruthenium, or manganese compound or a mixture thereof in water or a water-containing solvent mixture at a pH of from 7.5 to 13.

14. The process according to Claim 13 for preparing compounds of the formula (I) wherein for olefins of the formula (II) the substituents  $R^1$  to  $R^4$  are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, COO-aryl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, N-alkyl<sub>2</sub>, aryl, fluorine, chlorine, bromine, iodine, CHO, CF<sub>3</sub>, NHCO-alkyl, CONH<sub>2</sub>, CONH-alkyl, or NHCOO-alkyl.

15. The process according to Claim 13 wherein diols of the formula (I) in which  $R^1$  to  $R^4$  are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, aryl, fluorine, chlorine, bromine, CHO, or NHCO-alkyl are prepared.

16. The process according to Claim 13 wherein the oxidant is oxygen or a gas mixture comprising at least 15% by volume of oxygen.

17. The process according to Claim 13 wherein the catalyst is an osmium, ruthenium, or manganese compound.

18. The process according to Claim 13 wherein the reaction proceeds at a temperature of from 20 to 200°C and a pressure of up to 200 bar.

19. The process according to Claim 13 wherein an amine is added to improve selectivity.

20. A process according to Claim 19 wherein the amine is a tertiary amine.

21. A process according to Claim 19 wherein the amine is a bicyclic amine of the quinuclidine type.

22. The process according to Claim 13 wherein a sulfonamide is added as a cocatalyst.

23. The process according to Claim 22 wherein the sulfonamide cocatalyst is a methylsulfonamide and/or a carboxamide.

24. The process according to Claim 13 wherein the osmium compounds  $\text{OsO}_4$ ,  $\text{K}_2\text{Os}_2(\text{OH})_4$ ,  $\text{Na}_2\text{Os}_2(\text{OH})_4$ ,  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{OsCl}_3$ ,  $\text{H}_2\text{OsCl}_6$ ,  $[\text{CF}_3\text{SO}_3\text{Os}(\text{NH}_3)_5](\text{O}_3\text{SCF}_3)_2$ ,  $\text{OsO}_4$  on vinylpyridine, or  $\text{Bu}^t\text{NOsO}_3$  are used as catalysts and/or catalyst precursors.

25. The process according to Claim 13 wherein the manganese compounds  $\text{MnO}_2$ ,  $\text{KMnO}_4$ ,  $\text{Ca}(\text{MnO}_4)_2$ ,  $\text{MnCl}_3$ , or  $\text{Mn}(\text{OAc})_3$  are used as catalysts and/or catalyst precursors.

26. The process according to Claim 13 wherein the ruthenium compounds  $\text{RuCl}_3$ ,  $\text{RuO}_4$ , or  $\text{RuO}_2$  are used as catalysts and/or catalyst precursors.

27. The process according to Claim 13 wherein the catalyst is used in amounts of from 0.2 to 0.00001 equivalents, based on the olefin.

28. The process according to Claim 13 wherein the ratio of amine to metal is from 0.01:1 to 1 000:1.--

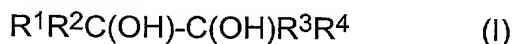
IN THE ABSTRACT:

Please add an Abstract as new page 21 to read as follows:

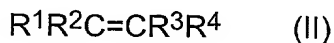
--METHOD FOR THE DIHYDROXYLATION OF  
OLEFINS USING TRANSITION METAL CATALYSTS

ABSTRACT OF THE DISCLOSURE

This invention relates to process for dihydroxylation of olefins using transition metal catalysts to obtain monofunctional, bifunctional, and/or polyfunctional 1,2-diols of the formula (I)



where  $\text{R}^1$  to  $\text{R}^4$  are defined herein, by reacting an olefin of the formula (II)



where  $\text{R}^1$  to  $\text{R}^4$  are defined as for formula (I),

with molecular oxygen in the presence of an osmium, ruthenium, or manganese compound in water or a water-containing solvent mixture at a pH of from 7.5 to 13.--

**REMARKS**

Applicants hereby offer preliminary amendments to the present application to place the application in better form for allowance.

Applicants have canceled Claims 1-12 in favor of replacement Claims 13-28 to correct certain informalities (including avoidance of multiple dependencies, avoidance of use claims, and removal of preferences or addition of new claims directed to such preferences) and to clarify the intended meaning of the claims. Applicants respectfully submit that the claims are fully supported in the specification.

Applicants have amended the specification to change the title to correspond to the English version of the title appearing on the International Application and to capitalize all letters in the title. Applicants submit that these amendments serve only to clarify their application and do not alter the scope of their disclosure.

Applicants have added an Abstract that summarizes the subject matter of their invention. A copy of the new Abstract is separately attached.

In view of the preceding amendments and remarks, allowance of the claims is respectfully requested.

Respectfully submitted,

By Richard E.L. Henderson  
Richard E.L. Henderson  
Attorney for Applicants  
Reg. No. 31,619

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Pittsburgh, Pennsylvania 15205-9741  
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/vjt/RH8500

ANNOTATED VERSION OF AMENDMENTSIN THE SPECIFICATION:

The title at page 1, line 1, has been changed from "Process for the dihydroxylation of olefins by means of transition metal catalysts" to

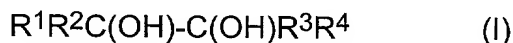
--METHOD FOR THE DIHYDROXYLATION OF  
OLEFINS USING TRANSITION METAL CATALYSTS --

IN THE CLAIMS:

The heading for the claims at page 18, line 1, has been changed from "Claims" to --WHAT IS CLAIMED IS:--.

Claims 1-12 have been canceled in favor of replacement Claims 13-28.

--13. A process for the dihydroxylation of olefins using transition metal catalysts to obtain monofunctional, bifunctional, and/or polyfunctional 1,2-diols of the formula (I)



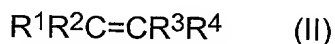
where

R<sup>1</sup> to R<sup>4</sup> are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, COO-aryl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, O-CO-aryl, O-CO-alkyl, OCOO-alkyl, N-alkyl<sub>2</sub>, NH-alkyl, N-aryl<sub>2</sub>, NH-aryl, NO, NO<sub>2</sub>, NOH, aryl, fluorine, chlorine, bromine, iodine, Si-alkyl<sub>3</sub>, CHO, SO<sub>3</sub>H, SO<sub>3</sub>-alkyl, SO<sub>2</sub>-alkyl, SO-alkyl, CF<sub>3</sub>, NHCO-alkyl, CONH<sub>2</sub>, CONH-alkyl, NHCOH, NHCOO-alkyl, CHCHCO<sub>2</sub>-alkyl, CHCHCO<sub>2</sub>H, PO-(aryl)<sub>2</sub>, PO(alkyl)<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, or PO(O-alkyl)<sub>2</sub>, where alkyl is a linear, branched, and/or cyclic aliphatic organic group having from 1 to 18 carbon atoms and aryl is a 5-, 6-, or 7-membered aromatic ring containing from 4 to 14 carbon atoms and from 0 to 3 heteroatoms and is optionally fused, and where the alkyl and/or the aryl group optionally bears up to six substituents selected independently from the group consisting of hydrogen, alkyl, O-alkyl, OCO-alkyl, O-aryl, aryl, fluorine, chlorine, bromine, iodine, OH, NO<sub>2</sub>, NO, Si-alkyl<sub>3</sub>, CN, COOH, CHO, SO<sub>3</sub>H,



NH<sub>2</sub>, NH-alkyl, N-alkyl<sub>2</sub>, PO-alkyl<sub>2</sub>, SO<sub>2</sub>-alkyl, SO-alkyl, CF<sub>3</sub>, NHCO-alkyl, COO-alkyl, CONH<sub>2</sub>, CO-alkyl, NHCOH, NHCOO-alkyl, CO-aryl, COO-aryl, PO-aryl<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, PO(O-alkyl)<sub>2</sub>, and SO<sub>3</sub>-alkyl, where alkyl and aryl are as defined above,

comprising reacting an olefin of the formula (II)



where R<sup>1</sup> to R<sup>4</sup> are defined as for formula (I),

with molecular oxygen in the presence of an osmium, ruthenium, or manganese compound or a mixture thereof in water or a water-containing solvent mixture at a pH of from 7.5 to 13.

14. The process according to Claim 13 for preparing compounds of the formula (I) wherein for olefins of the formula (II) the substituents R<sup>1</sup> to R<sup>4</sup> are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, COO-aryl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, N-alkyl<sub>2</sub>, aryl, fluorine, chlorine, bromine, iodine, CHO, CF<sub>3</sub>, NHCO-alkyl, CONH<sub>2</sub>, CONH-alkyl, or NHCOO-alkyl.

15. The process according to Claim 13 wherein diols of the formula (I) in which R<sup>1</sup> to R<sup>4</sup> are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, aryl, fluorine, chlorine, bromine, CHO, or NHCO-alkyl are prepared.

16. The process according to Claim 13 wherein the oxidant is oxygen or a gas mixture comprising at least 15% by volume of oxygen.

17. The process according to Claim 13 wherein the catalyst is an osmium, ruthenium, or manganese compound.

18. The process according to Claim 13 wherein the reaction proceeds at a temperature of from 20 to 200°C and a pressure of up to 200 bar.

19. The process according to Claim 13 wherein an amine is added to improve selectivity.

20. A process according to Claim 19 wherein the amine is a tertiary amine.

21. A process according to Claim 19 wherein the amine is a bicyclic amine of the quinuclidine type.

22. The process according to Claim 13 wherein a sulfonamide is added as a cocatalyst.

23. The process according to Claim 22 wherein the sulfonamide cocatalyst is a methylsulfonamide and/or a carboxamide.

24. The process according to Claim 13 wherein the osmium compounds  $\text{OsO}_4$ ,  $\text{K}_2\text{Os}_2(\text{OH})_4$ ,  $\text{Na}_2\text{Os}_2(\text{OH})_4$ ,  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{OsCl}_3$ ,  $\text{H}_2\text{OsCl}_6$ ,  $[\text{CF}_3\text{SO}_3\text{Os}(\text{NH}_3)_5](\text{O}_3\text{SCF}_3)_2$ ,  $\text{OsO}_4$  on vinylpyridine, or  $\text{Bu}^t\text{NOsO}_3$  are used as catalysts and/or catalyst precursors.

25. The process according to Claim 13 wherein the manganese compounds  $\text{MnO}_2$ ,  $\text{KMnO}_4$ ,  $\text{Ca}(\text{MnO}_4)_2$ ,  $\text{MnCl}_3$ , or  $\text{Mn}(\text{OAc})_3$  are used as catalysts and/or catalyst precursors.

26. The process according to Claim 13 wherein the ruthenium compounds  $\text{RuCl}_3$ ,  $\text{RuO}_4$ , or  $\text{RuO}_2$  are used as catalysts and/or catalyst precursors.

27. The process according to Claim 13 wherein the catalyst is used in amounts of from 0.2 to 0.00001 equivalents, based on the olefin.

28. The process according to Claim 13 wherein the ratio of amine to metal is from 0.01:1 to 1 000:1.--

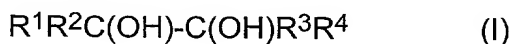
#### **IN THE ABSTRACT:**

An Abstract has been added as new page 21 as follows:

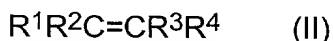
#### **--METHOD FOR THE DIHYDROXYLATION OF OLEFINS USING TRANSITION METAL CATALYSTS**

#### **ABSTRACT OF THE DISCLOSURE**

This invention relates to process for dihydroxylation of olefins using transition metal catalysts to obtain monofunctional, bifunctional, and/or polyfunctional 1,2-diols of the formula (I)



where  $\text{R}^1$  to  $\text{R}^4$  are defined herein, by reacting an olefin of the formula (II)



where  $\text{R}^1$  to  $\text{R}^4$  are defined as for formula (I),

with molecular oxygen in the presence of an osmium, ruthenium, or manganese compound in water or a water-containing solvent mixture at a pH of from 7.5 to 13.--

10/019996

531 Rec'd PCT

19 OCT 2001

Process for the dihydroxylation of olefins by means of transition metal catalysts

The present invention relates to a process for preparing 1,2-diols from olefins using catalysts based on transition metal compounds.

1,2-Diols, in particular cis-1,2-diols, are of industrial importance as fine chemicals, solvents, starting materials for polyesters and other polymers, and also as intermediates for agrochemicals. Propylene glycol and ethylene glycol in particular are of extraordinary importance as bulk chemicals. Numerous 1,2-diols are also of commercial interest for the preparation of pharmaceuticals, cosmetics, cleaners and are employed in the textiles and plastics industries. In many cases, the carboxylic esters display a constant viscosity over a wide temperature range, combined with a high boiling point. They are good synthetic lubricants and plasticizers.

A frequently employed method of synthesizing 1,2-diols in the university sector are "dihydroxylation reactions" such as the Sharpless dihydroxylation reaction in which olefins are reacted in the presence of osmium tetroxide and an oxidant. Review articles which describe this methodology may be found, for example, in "*Asymmetric Dihydroxylation Reactions*" M. Beller, K. B. Sharpless, in B. Cornils, W.A. Herrmann (Eds.), VCH, 1996, Weinheim, and H.C. Kolb, M.S. Van Nieuwenhze, K.B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483.

From an industrial point of view, olefins are available in virtually unlimited quantities as a source for the synthesis of diols, so that metal-catalyzed dihydroxylation reactions could in principle be used for the preparation of commercially interesting products such as propylene glycol and also fine chemicals such as 1,2-pentanediol and pinacol. Although catalytic oxidation processes are frequently superior in ecological terms to stoichiometric oxidation processes, the abovementioned products are at present produced predominantly via noncatalytic multistate processes, e.g. stoichiometric reactions with peracids or hydrogen peroxide and subsequent hydrolysis of the epoxide formed as an intermediate. This is due to

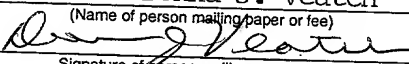
"Express Mail" mailing label number LT671450313US

Date of Deposit October 19, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)

  
Signature of person mailing paper or fee

the known reoxidants for manganese, ruthenium and osmium oxides being too expensive for an industrial preparation of fine and bulk chemicals and only allowing the economical preparation of extremely high-priced pharmaceutical intermediates.

- 5 The dialcohols can be synthesized stoichiometrically from olefins by reaction with  $\text{KMnO}_4$  (A.J. Fatiadi, *Synthesis* 1984, 85-127; W.P. Weber, J.P. Shepard, *Tetrahedron Lett.* 1972, 48, 4907-4908; E. Salamci, H. Segan, Y. Sütbeyaz, M. Balci; *J. Org. Chem.* 1997, 62, 2453-2557; B.G. Hazra, T.P. Kumar, P.L. Joshi, *Liebigs Ann. Chem.* 1997, 1029-1034).  $\text{RuO}_4$  gives dialcohols by stoichiometric  
10 reaction of olefins (L. Albarella, V. Piccialli, D. Smaldone, D. Sica, *J. Chem. Res.* 1996, 9, 400-401) and by means of catalytic reaction using  $\text{NaIO}_4$  as reoxidant (T.K.M. Shing, E.K.W. Tam, V.W.F. Tai, I.H.F. Chung, Q. Jiang, *Chem. Eur. J.* 1996, 2, 50-57; T. Sugai, H. Okazaki, A. Kuboki, H. Ohta, *Bull. chem. Soc. Jpn.* 1997, 70, 2535-2540; J. Angermann, K. Homann, H.-U. Reissig, R. Zimmer *Synlett*  
15 1995, 1014-1016; M. Desjardins, L. Brammer Jr., T. Hudlicky, *Carbohydrate Res.* 1997, 504, 39-42; M. J. Mulvihill, M.J. Miller, *Tetrahedron* 1998, 54, 6625-6626). Initial work on dihydroxylation by means of osmium oxide involved stoichiometric reactions (O. Makowka, *Chem. Ber.* 1908, 45, 943; R. Criegee, *Liebigs Ann. Chem.* 1936, 522, 75; R. Criegee, *Angew. Chem.* 1937, 50, 153). Reactions using catalytic  
20 amounts of osmium tetroxide and chlorates as reoxidants (K.A. Hoffmann, *Chem.* 1912, 45, 3329) or  $\text{H}_2\text{O}_2$  in tert-butanol (N.A. Milas, J.-H. Trepagnier, J.T. Nolan, M. Ji. Iliopolus, *J. Am. Chem. Soc.* 1959, 81, 4730) as reoxidant lead to overoxidation of the diols formed. Use of  $\text{H}_2\text{O}_2$  results in formation of peroxosmic acid  $\text{H}_2\text{O}_2\text{O}_6$  which cleaves the diol formed as an intermediate and leads to carbonyl  
25 compounds. To reduce the overoxidation, tert-butyl hydroperoxide in the presence of  $\text{Et}_4\text{NOH}$  (K.B. Sharpless, K. Akashi, *J. Am. Chem. Soc.* 1976, 98, 1986; P.H.J. Carlsen, T. Katsuki, V.S. Martin, K.B. Sharpless, *J. Org. Chem.* 1981, 46, 3936; F.X. Webster, J. Rivas-Enterrios, R.M. Silverstein, *J. Org. Chem.* 1987, 52, 689; V.S. Martin, M.T. Nunez, C.E. Tonn, *Tetrahedron Lett.* 1988, 29, 2701; M. Caron, P.R. Carlier, K.B. Sharpless, *J. Org. Chem.* 1988, 53, 5185), tertiary amine oxides and in  
30 most cases N-methylmorpholine N-oxide (NMO; Upjohn Process) (W.P. Schneider,

A.V. McIntosh, US 2,769,824 (1956); V. Van Rheenen, R.C. Kelly, D.Y. Cha, *Tetrahedron Lett.* **1976**, 17, 1973) are used as reoxidants. Trimethylamine oxide is superior to NMO for trisubstituted and sometimes also tetrasubstituted alkenes (R. Ray, D.S. Matteson, *Tetrahedron Lett.* **1980**, 21, 449). Despite the selective and catalytic dihydroxylation which is possible using N-oxides, the price of these reoxidants is prohibitive for relatively large-scale industrial applications.

In recent years,  $\text{Na}_3[\text{Fe}(\text{CN})_6]$  in the presence of sodium carbonate in a 2-phase system has been used very successfully as reoxidant for  $\text{OsO}_4$  (M. Minato, K. Yamamoto, J. Tsuji, *J. Org. Chem.* **1990**, 55, 766; M.P. Singh, H.S. Singh, B.S. Arya, A.K. Singh, A.K. Sisodia, *Indian J. Chem.* **1975**, 13, 112), particularly also in enantioselective dihydroxylation (Y. Ogino, H. Chen, H.L. Kwong, K.B. Sharpless, *Tetrahedron Lett.* **1991**, 32, 3965). Significant disadvantages for the synthesis of the diols on a relatively large scale are again the price and the superstoichiometric amount of iron complex to be used (3 mol = 990 g per 1 mol of substrate) with addition of potassium carbonate (3 mol = 420 g). In the case of processes for the electrochemical oxidation of the  $\text{Na}_4[\text{Fe}(\text{CN})_6]$  formed in the reaction to give  $\text{Na}_3[\text{Fe}(\text{CN})_6]$  (Sepracor Inc. (Y. Gao, C.M. Zepp), PCT Int. Appl. WO 9 317 150, 1994; Anon., *Chem. Eng. News.* **1994**, 72 (24), 41), too, industrial implementation is difficult since electrochemical processes are generally too expensive because of the apparatus required.

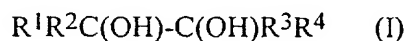
To circumvent the disadvantages of the abovementioned reoxidants, attempts have been made in the past to use air or oxygen for the reoxidation of  $\text{Os}^{\text{VI}}$  to  $\text{Os}^{\text{VIII}}$ . Such a process is the most attractive method from economic and ecological points of view. However, Cairns *et al.* have shown that no 1,2-dialcohol is observed in the reaction of allyl alcohol, ethylene, cyclohexene and styrene in the presence of  $\text{OsO}_4$  and oxygen, but in all cases overoxidation results in formation of industrially unusable amounts of the corresponding carboxylic acids, e.g. benzoic acid (styrene as substrate) and  $\text{CO}_2$  (J.F. Cairns, H.L. Roberts, *J. Chem. Soc. (C)* **1968**, 640). In a process of Celanese Corporation (GB-B 1.028.940), too, only formic acid and

heptanoic acid are obtained from 1-octene. Even in the reaction of the less oxidation-sensitive ethylene, the 1,2-diol is obtained only in traces (2% of glycol after 4 hours at an O<sub>2</sub>-pressure of 7 MPa). Employees of *Exxon* utilize bimetallic systems comprising OsO<sub>4</sub> and Cu(II) salts (US-A 4 496 779, EP-B 0 077 201, R.G. Austin, R.C. Michaelson, R.S. Myers in *Catalysis in Organic Reactions* (Ed: R.L. Augustine), Marcel Dekker, New York 1985, p. 269). In a manner analogous to the Wacker process, Os<sup>VI</sup> is reoxidized by the Cu salt which is then oxidized again by means of O<sub>2</sub>. In this process, maximum conversions of propylene are 3-5% after a reaction time of 2 hours and a pressure of 28 bar.

In summary, it can be seen that the known methods for reoxidizing osmium, ruthenium and manganese by means of molecular oxygen are not usable in dihydroxylation reactions for synthesizing dialcohols.

To avoid the abovementioned disadvantages of the known catalytic processes, it is an object of the invention to develop a novel process for metal-catalyzed dihydroxylation which is simple to carry out and gives 1,2-diols in high yield and purity, with molecular oxygen being used as reoxidant, and is suitable for industrial implementation.

This object is achieved by a process for the dihydroxylation of olefins by means of transition metal catalysts in which, according to the invention, monofunctional, bifunctional and polyfunctional 1,2-diols of the formula I,

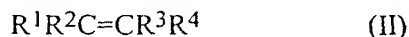


where

R<sup>1</sup> to R<sup>4</sup> are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, COO-aryl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, O-CO-aryl, O-CO-alkyl, OCOO-alkyl, N-alkyl<sub>2</sub>, NH-alkyl, N-aryl<sub>2</sub>, NH-aryl, NO, NO<sub>2</sub>, NOH, aryl.

fluorine, chlorine, bromine, iodine, NO<sub>2</sub>, Si-alkyl<sub>3</sub>, CHO, SO<sub>3</sub>H, SO<sub>3</sub>-alkyl, SO<sub>2</sub>-alkyl, SO-alkyl, CF<sub>3</sub>, NHCO-alkyl, CONH<sub>2</sub>, CONH-alkyl, NHCOH, NHCOO-alkyl, CHCHCO<sub>2</sub>-alkyl, CHCHCO<sub>2</sub>H, PO-(aryl)<sub>2</sub>, PO-(alkyl)<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, PO(O-alkyl)<sub>2</sub>, where alkyl represents an aliphatic organic group having from 1 to 18 carbon atoms which may be linear, branched and/or cyclic and aryl is a 5-, 6- or 7-membered aromatic ring which contains from 4 to 14 carbon atoms and may be fused and contain from 0 to 3 heteroatoms such as N, O, S and where the alkyl and/or the aryl group may bear up to six further substituents selected independently from among hydrogen, alkyl, O-alkyl, OCO-alkyl, O-aryl, aryl, fluorine, chlorine, bromine, iodine, OH, NO<sub>2</sub>, NO, Si-alkyl<sub>3</sub>, CN, COOH, CHO, SO<sub>3</sub>H, NH<sub>2</sub>, NH-alkyl, N-alkyl<sub>2</sub>, PO-alkyl<sub>2</sub>, SO<sub>2</sub>-alkyl, SO-alkyl, CF<sub>3</sub>, NHCO-alkyl, COO-alkyl, CONH<sub>2</sub>, CO-alkyl, NHCOH, NHCOO-alkyl, CO-aryl, COO-aryl, PO-aryl<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, PO(O-alkyl)<sub>2</sub>, SO<sub>3</sub>-alkyl, where alkyl and aryl are as defined above,

are obtained by reacting olefins of the formula II



where

R<sup>1</sup> to R<sup>4</sup> are as defined above, with molecular oxygen in the presence of an osmium, ruthenium or manganese compound or a mixture thereof in water or a water-containing solvent mixture at a pH of from 7.5 to 13.

In particular, compounds of the formula I are prepared using olefins of the formula II in which the substituents R<sup>1</sup> to R<sup>4</sup> are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, COO-aryl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, N-alkyl<sub>2</sub>, aryl, fluorine, chlorine, bromine, iodine, CHO, CF<sub>3</sub>, NHCO-alkyl, CONH<sub>2</sub>, CONH-alkyl, NHCOO-alkyl. Here, alkyl and aryl are as defined above.

Particular preference is given to a process in which diols of the formula I in which R<sup>1</sup> to R<sup>4</sup> are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, aryl, fluorine, chlorine, bromine, CHO, NHCO-alkyl, are prepared. Here, alkyl and aryl are as defined above.

5

The process of the invention is carried out in the presence of water. It has been found to be advantageous to add a further organic solvent in addition to the olefin. The process of the invention can, in the case of various olefins, also be carried out in an olefin-water mixture without further solvent. Further solvents used are generally inert organic solvents. Suitable solvents are aliphatic ethers, aromatic or aliphatic hydrocarbons, alcohols and esters, halogenated hydrocarbons, dipolar aprotic solvents such as dialkyl sulfoxides, N,N-dialkylamides of aliphatic carboxylic acids and also mixtures thereof. Preference is given to alcohols, esters and ethers. As aqueous phase, use is generally made of a basic aqueous solution having a pH of from 7.5 to 13. The basic pH of the solution is achieved by addition of a base to the water. It is generally advantageous to carry out the reaction in buffered aqueous solutions, preferably having a pH of from 8 to 13. The buffered solution is prepared by addition of known buffers to water.

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To enable the diol products to be separated off readily, it is sometimes advantageous to use an aqueous salt solution or a buffered aqueous salt solution, for example an aqueous solution of an alkali metal halide or alkaline earth metal halide, as solvent in place of water or buffered aqueous solutions.

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In the process of the invention, molecular oxygen or a gas mixture comprising molecular oxygen is used as oxidant. Preference is given to gas mixtures comprising at least 15% by volume of oxygen. Particular preference is given to air and oxygen gas having an oxygen content of <95 %.

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The reaction preferably proceeds at temperatures of from 20 to 200°C. in many cases, it has been found to be useful to employ temperatures of from 30 to 150°C.



preferably from 40 to 100°C. The process of the invention can be carried out under atmospheric pressure, e.g. by passing oxygen through the reaction solution. However, the reaction rate is increased when a superatmospheric oxygen pressure is employed. The process can be carried out at pressures of up to 200 bar, but is usually carried out at a pressure of up to 60 bar and preferably in the range from atmospheric pressure to 20 bar.

To achieve selectivity of the dihydroxylation reaction, the catalyst is activated by addition of an amine. Amines suitable for this purpose are, in particular, tertiary amines such as trialkylamines, dialkylarylamines, alkyl diarylamines, which may be cyclic and/or linear, pyridines and quinolones. Preference is given to bicyclic amines such as 1,4-diazabicyclo[2,2,2]octane and also compounds of the quinuclidine type and substituted phthalazines, diphenylpyrimidines and carbamoylindolines.

The transition metal catalysts used are generally oxides of the elements osmium, manganese and ruthenium, preferably osmium. These metals are generally used in oxidation states of  $> +4$ . However, it is also possible to use catalyst precursors in lower oxidation states. These are converted under the reaction conditions into the catalytically active Os(VIII) and Os(VI) species or Mn(VII) or Ru(VIII) species. Examples of osmium catalysts or catalyst precursors which can be used are:  $\text{OsO}_4$ ,  $\text{K}_2\text{Os}_2(\text{OH})_4$ ,  $\text{Na}_2\text{Os}_2(\text{OH})_4$ ,  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{OsCl}_3$ ,  $\text{H}_2\text{OsCl}_6$ ,  $[\text{CF}_3\text{SO}_3\text{Os}(\text{NH}_3)_5](\text{O}_3\text{SCF}_3)_2$ ,  $\text{OsO}_4$  on vinylpyridine,  $\text{Bu}^t\text{NOsO}_3$ . Examples of manganese catalysts or catalyst precursors which can be used are:  $\text{MnO}_2$ ,  $\text{KMnO}_4$ ,  $\text{Ca}(\text{MnO}_4)_2$ ,  $\text{MnCl}_3$ ,  $\text{Mn}(\text{OAc})_3$ . Examples of ruthenium catalysts or catalyst precursors which can be used are:  $\text{RuCl}_3$ ,  $\text{RuO}_4$ ,  $\text{RuO}_2$ .

In the process of the invention, the catalyst is used in catalytic amounts relative to the olefin. In general, use is made of from 0.2 to 0.00001 equivalents, based on olefin, preferably from 0.1 to 0.0001 equivalents and particularly preferably from 0.1 to 0.0005 equivalents. The ratio of amine to metal is from 0.01:1 to 1:000:1, preferably

from 0.1:1 to 100:1. Particular preference is given to using ratios of amine to osmium of from 1:1 to 50:1.

When using bulky olefins, in particular trisubstituted and tetrasubstituted olefins, it is sometimes advantageous to add a cocatalyst to hydrolyze the metal ester formed as an intermediate. This cocatalyst is an amide which aids hydrolysis, for example a sulfonamide or/and carboxamide. Particular preference is given to the addition of methylsulfonamide.

The cocatalyst is used in an amount of from 0.01 mol% to 10 mol% (based on olefin), preferably from 0.1 to 5 mol%.

The particular advantage of the process of the invention is the use of oxygen or oxygen-containing gases as reoxidant. Despite the comparatively difficult reoxidation process, high catalyst productivities can be achieved by mixing the aqueous catalyst phase which has been used once with olefin again. In this way, the catalyst costs for the process of the invention are minimized, so that even industrial processes can be carried out economically.

The process of the invention is particularly surprising and novel since no catalyzed, selective dihydroxylation reactions to form 1,2-diols using oxygen as reoxidant have been described in the past. This is attributable to the few previous studies using oxygen as reoxidant leading essentially to overoxidation, if any reaction at all occurred. The novel combination described in the process of the invention of addition of a ligand which accelerates the dihydroxylation and carrying out the process in a buffered basic solution surprisingly leads to a chemoselective dihydroxylation process even in the presence of oxygen. The process of the invention shows for the first time that the statements in the known literature on the catalyzed dihydroxylation using oxygen are wrong.

The particular advantages of the novel process are the price advantage of the oxidant, the simple way in which the process can be carried out and the high selectivity of the process compared with other oxidants which have been employed.

5 The 1,2-diols prepared according to the invention can be used, inter alia, as solvents, starting materials for polyesters and other polymers, intermediates for agrochemicals, cosmetics, cleaners and are employed in the form of their esters as synthetic lubricants and plasticizers.

10 The following examples illustrate the process of the invention without restricting it to the specific examples presented.

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## Examples

### Example 1

5 18.4 mg of  $K_2OsO_4 \times 2H_2O$  (0.05 mmol) are weighed into a Schlenk vessel. While stirring by means of a magnetic stirrer, 25 ml of 0.4-0.5 molar  $Na_3PO_4/Na_2HPO_4$  buffer solution having a pH of 11.2 and 10 ml of 2-methyl-2-propanol are added, resulting in formation of 2 phases. The vessel is heated to 50°C on a water bath and  
10 flushed with oxygen. After addition of 173  $\mu$ l of styrene (1.5 mmol), the reaction vessel is connected to a burette filled with oxygen, and the reaction solution is stirred at 50°C under a slightly superatmospheric  $O_2$  pressure (about 50 cm of water) for 24 hours.

15 The reaction mixture is worked up as described below:

2 g of sodium bisulfite and 10 ml of ethyl acetate are added to the reaction solution. After stirring for 10 minutes, the upper organic phase is separated off and the aqueous phase is shaken with 10 ml of ethyl acetate. The organic phases are purified, dried over anhydrous sodium sulfate and evaporated to dryness on a rotary  
20 evaporator.

This gives 130 mg of (R)/(S)-1-phenyl-1,2-ethanediol, 63% (based on styrene).

To isolate any acidic products formed, the aqueous solution is acidified and shaken twice with 15 ml each time of ether. This gives 20 mg of a crystalline product, of  
25 which more than 90% is made up by benzoic acid.

### Example 2

30 18.4 mg of  $K_2OsO_4 \times 2H_2O$  (0.05 mmol) are weighed into a Schlenk vessel. While stirring by means of a magnetic stirrer, 25 ml of 0.3 molar borax NaOH buffer solution having a pH of 10.2, 4 g of NaCl and 10 ml of 2-methyl-2-propanol are

added. 2 phases are formed. The vessel is heated to 50°C on a water bath and flushed with oxygen. After addition of 288 µl of styrene (2.5 mmol), the reaction vessel is connected to a burette filled with oxygen, and the reaction solution is stirred at 50°C under a slightly superatmospheric O<sub>2</sub> pressure (50 cm of water) for 24 hours. The reaction mixture is worked up as described in example 1.

This gives 215 mg of (R)/(S)-1-phenyl-1,2-ethanediol (62%) and 101 mg of benzoic acid.

### Example 3

1.5 mmol of styrene are reacted as described in example 1, but the reaction temperature was 30°C and the reaction time was 62 hours. After work-up, this gives 104 mg of (R)/(S)-1-phenyl-1,2-ethanediol (50%) and 15 mg of benzoic acid.

### Example 4

The procedure of example 1 is repeated, but 0.05 mmol of 1,4-diazabicyclo[2.2.2]octane are added to the osmium salt. This gives 151 mg of (R)/(S)-1-phenyl-1,2-ethanediol (72%) and 31 mg of benzoic acid.

### Example 5

The procedure of example 1 is repeated using 231 mg of 2-vinylnaphthalene (1.5 mmol) as substrate. As a difference from example 1, the reaction time was 7 hours. After work-up, this gives 214 mg of (R)/(S)-1-(2-naphthyl)-1,2-ethanediol (76%). 34 mg of a crystalline product consisting predominantly of 2-naphthalene-carboxylic acid are obtained from the ether solution.

Example 6

5 Using a method analogous to example 1, 18.4 mg of  $K_2OsO_4 \times 2H_2O$  (0.05 mmol) are reacted with 130  $\mu$ l (1 mmol) of  $\alpha$ -methylstyrene in the 2-phase system described.

After work-up in the manner indicated, this gives 110 mg of (R)/(S)-2-phenyl-1,2-propanediol (72%).

10 Example 7

Using a method analogous to example 1, 18.4 mg of  $K_2OsO_4 \times 2H_2O$  (0.05 mmol) are reacted with 130  $\mu$ l (1 mmol) of trans- $\beta$ -methylstyrene.

15 After the usual work-up, this gives 108 mg of 1-phenyl-1,2-propanediol (71%).

Example 8

20 Using a method analogous to example 1, 18.4 mg of  $K_2OsO_4 \times 2H_2O$  (0.05 mmol) are reacted with 203  $\mu$ l (2 mmol) of cyclohexene.

After the usual work-up, this gives 196 mg of cis-cyclohexanediol (84%).

Example 9

25 7.4 mg of  $K_2OsO_4 \times 2H_2O$  (0.02 mmol) are weighed into a Schlenk vessel. While stirring by means of a magnetic stirrer, 25 ml of a buffer solution having a pH of 10.4 and prepared from 0.5 molar  $K_2HPO_4$  solution and 2 molar NaOH, together with 10 ml of 2-methyl-2-propanol are added, resulting in formation of 2 phases. The  
30 vessel is heated to 50°C on a water bath and flushed with oxygen. After addition of 230  $\mu$ l of styrene (2 mmol), the reaction vessel is connected to a burette filled with

- 13 -

oxygen, and the reaction solution is stirred at 50°C under a slightly super-atmospheric O<sub>2</sub> pressure (about 50 cm of water) for 24 hours.

The reaction mixture was worked up as described below:

2 g of sodium bisulfite and 20 ml of ethyl acetate are added to the reaction solution. After stirring for 10 minutes, the upper organic phase is separated off. Dialcohol and unreacted olefin are determined by means of GC.

Yield of 1-phenyl-1,2-ethanediol: 43% (selectivity: 57%).

#### Example 10

The procedure of example 9 is repeated, but 0.06 mmol of 1,4-diazabicyclo[2,2,2]octane are added to the osmium salt.

Yield of 1-phenyl-1,2-ethanediol: 43% (selectivity: 78%).

#### Example 11

The procedure of example 10 is repeated using 308 mg of 2-vinylnaphthalene (2 mmol) as substrate. Dialcohols and unreacted olefin are determined by means of HPLC in this case.

Yield of 1-(2-naphthyl)-1,2-ethanediol: 56% (selectivity: 75 %).

#### Example 12

7.4 mg of K<sub>2</sub>OsO<sub>4</sub> x 2H<sub>2</sub>O (0.02 mmol)/0.02 mmol of DABCO are reacted with 318 µl of 1-phenyl-1-cyclohexene (2 mmol) using the procedure described in example 9, but using a buffer solution having a pH of 11.2

Yield of 1-phenyl-1,2-cyclohexanediol: 81% (selectivity: 84%)

**Example 13**

3.7 mg of  $K_2OsO_4 \times 2H_2O$  (0.01 mmol) are reacted with 260  $\mu$ l of  $\alpha$ -methylstyrene (2 mmol) using the procedure described in example 9 but for a reaction time of 12 hours.

Yield of 2-phenyl-1,2-propanediol: 92% (selectivity: 92%).

**Example 14**

The procedure of example 13 is repeated, but 0.03 mmol of 1,4-diazabicyclo[2.2.2]octane are added to the osmium salt. Reaction time = 16 h.

Yield of 2-phenyl-1,2-propanediol: 98% (selectivity: 98%).

**Example 15**

Cyclohexane is reacted using a procedure analogous to example 14. Reaction time = 24 h.

Yield of 1,2-cyclohexanediol: 68% (selectivity: 75%).

**Example 16**

1-Octene is reacted using a procedure analogous to example 14. Reaction time = 15 h.

Yield of 1,2-octanediol: 96% (selectivity: 97%).

**Example 17**

1.9 mg of  $K_2OsO_4 \times 2H_2O$  (0.05 mmol) are reacted with 260  $\mu$ l of  $\alpha$ -methylstyrene (2 mmol) with addition of 0.015 mmol of 1,4-diazabicyclo[2.2.2]octane using the procedure described in example 9.

Yield of 2-phenyl-1,2-propanediol: 96% (selectivity: 96%).



**Example 18**

7.4 mg of  $K_2OsO_4 \times 2H_2O$  (0.02 mmol)/0.06 mmol of DABCO are reacted with 240  $\mu$ l of 1-methyl-1-cyclohexene (2 mmol) using the procedure described in example 9, but for a reaction time of 14 h and using a buffer solution having a pH of 11.2.

Yield of 1-methyl-1,2-cyclohexanediol: 78% (selectivity: 80%).

**Example 19**

320  $\mu$ l of allyltrimethylsilane (2 mmol) are reacted using a procedure analogous to example 18 but at a pH of 10.4.

Yield of 3-(trimethylsilyl)-1,2-propanediol: 72% (selectivity: 83%).

**Example 20**

14.7 mg of  $K_2OsO_4 \times 2H_2O$  (0.04 mmol)/0.12 mmol of DABCO are reacted with 380  $\mu$ l (2 mmol) of *trans*-5-decene using the procedure described in example 9, but for a reaction time of 18 h and using a buffer solution having a pH of 12.0.

Yield of 5,6-decanediol: 85% (selectivity: 96%).

**Example 21**

240  $\mu$ l of 2,3-dimethyl-2-butene (2 mmol) are reacted using a method analogous to example 20.

Yield of 2,3-dimethyl-2,3-butanediol: 99% (selectivity: 99%).

**Example 22**

245  $\mu$ l of 2-methyl-2-pentene (2 mmol) are reacted at pH = 11.2 using a method analogous to example 20.

Yield of 2-methyl-2,3-pentanediol: 88% (selectivity: 87%).

### Example 23

5 692 mg of 1H,1H,2H-perfluoro-1-octene (2 mmol) are reacted at pH = 10.4 using a method analogous to example 20.

Yield of 1H,1H,2H-perfluorooctane-1,2-diol: 53% (selectivity: 84%).

### Example 24

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245  $\mu$ l of 2-vinyl-1,3-dioxolane (2 mmol) are reacted using a procedure analogous to example 23.

Yield of 2-(1,2-dihydroxyethyl)-1,3-dioxolane: 59% (selectivity: 97%).

15

### Example 25

7.4 mg of  $K_2OsO_4 \times 2H_2O$  (0.02 mmol)/0.06 mmol of DABCO are reacted with 275  $\mu$ l of allyl phenyl ether (2 mmol) using the procedure described in example 9. Reaction time = 18 h.

20

Yield of 3-phenoxy-1,2-propanediol: 50% (selectivity: 96%).

### Example 26

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295  $\mu$ l of allyl phenyl sulfide (2 mmol) are reacted using a method analogous to example 25.

Yield of 2,3-dihydroxypropyl phenyl sulfide: 51% (selectivity: 94%)

### Example 27

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0.002 mmol of  $K_2OsO_4 \times 2H_2O$  dissolved in water, 0.006 mmol of DABCO and 25 ml of a buffer solution having a pH of 10.4 and prepared from 0.5 molar  $K_2HPO_4$

solution and 2 molar NaOH, together with 12 ml of 2-methyl-2-propanol are placed in a glass vessel located in an autoclave. The mixture is stirred by means of a magnetic stirrer and two phases are formed. After addition of 260  $\mu$ l of  $\alpha$ -methylstyrene (2 mmol), the autoclave is pressurized with 5 bar of oxygen and is heated to 50 - 55°C.

After 24 hours, the reaction mixture is worked up as described in example 9.

Yield of 2-phenyl-1,2-propanediol: 94% (selectivity: 94%).

#### Example 28

0.005 mmol of  $K_2OsO_4 \times 2H_2O$ /0.015 mmol of DABCO are reacted with 650  $\mu$ l of  $\alpha$ -methylstyrene (5 mmol) under an  $O_2$  pressure of 5 bar using the procedure described in example 27.

Yield of 3-phenyl-1,2-propanediol: 95% (selectivity: 95%).

#### Example 29

The procedure of example 27 is repeated, but the autoclave is pressurized with 5 bar of compressed air in place of pure oxygen.

Yield of 2-phenyl-1,2-propanediol: 41% (selectivity: 93%).

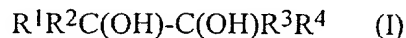
#### Example 30

The procedure of example 29 is repeated, but the autoclave is pressurized with 10 bar of compressed air.

Yield of 2-phenyl-1,2-propanediol: 76% (selectivity: 92%).

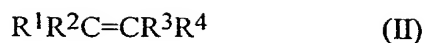
# Claims

1. A process for the dihydroxylation of olefins by means of transition metal catalysts to prepare monofunctional, bifunctional or/and polyfunctional 1,2-diols of the formula I,



where

$R^1$  to  $R^4$  are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, COO-aryl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, O-CO-aryl, O-CO-alkyl, OCOO-alkyl, N-alkyl<sub>2</sub>, NH-alkyl, N-aryl<sub>2</sub>, NH-aryl, NO, NO<sub>2</sub>, NOH, aryl, fluorine, chlorine, bromine, iodine, NO<sub>2</sub>, Si-alkyl<sub>3</sub>, CHO, SO<sub>3</sub>H, SO<sub>3</sub>-alkyl, SO<sub>2</sub>-alkyl, SO-alkyl, CF<sub>3</sub>, NHCO-alkyl, CONH<sub>2</sub>, CONH-alkyl, NHCOH, NHCOO-alkyl, CHCHCO<sub>2</sub>-alkyl, CHCHCO<sub>2</sub>H, PO-(aryl)<sub>2</sub>, PO-(alkyl)<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, PO(O-alkyl)<sub>2</sub>, where alkyl represents an aliphatic organic group having from 1 to 18 carbon atoms which may be linear, branched and/or cyclic and aryl is a 5-, 6- or 7-membered aromatic ring which contains from 4 to 14 carbon atoms and may be fused and contain from 0 to 3 heteroatoms such as N, O, S and where the alkyl and/or the aryl group may bear up to six further substituents selected independently from among hydrogen, alkyl, O-alkyl, OCO-alkyl, O-aryl, aryl, fluorine, chlorine, bromine, iodine, OH, NO<sub>2</sub>, NO, Si-alkyl<sub>3</sub>, CN, COOH, CHO, SO<sub>3</sub>H, NH<sub>2</sub>, NH-alkyl, N-alkyl<sub>2</sub>, PO-alkyl<sub>2</sub>, SO<sub>2</sub>-alkyl, SO-alkyl, CF<sub>3</sub>, NHCO-alkyl, COO-alkyl, CONH<sub>2</sub>, CO-alkyl, NHCOH, NHCOO-alkyl, CO-aryl, COO-aryl, PO-aryl<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, PO(O-alkyl)<sub>2</sub>, SO<sub>3</sub>-alkyl, where alkyl and aryl are as defined above, characterized in that olefins of the formula II



where

R<sup>1</sup> to R<sup>4</sup> are as defined above, are reacted with molecular oxygen in the presence of an osmium, ruthenium or manganese compound or a mixture thereof in water or a water-containing solvent mixture at a pH of from 7.5 to 13.

2. The process as claimed in claim 1 for preparing compounds of the formula I, characterized in that olefins of the formula II in which the substituents R<sup>1</sup> to R<sup>4</sup> are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, COO-aryl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, N-alkyl<sub>2</sub>, aryl, fluorine, chlorine, bromine, iodine, CHO, CF<sub>3</sub>, NHCO-alkyl, CONH<sub>2</sub>, CONH-alkyl, NHCOO-alkyl, where alkyl and aryl are as defined above, are used.
3. The process as claimed in claim 1 or 2, characterized in that diols of the formula I in which R<sup>1</sup> to R<sup>4</sup> are each, independently of one another, hydrogen, alkyl, CN, COOH, COO-alkyl, CO-alkyl, CO-aryl, O-alkyl, O-aryl, aryl, fluorine, chlorine, bromine, CHO, NHCO-alkyl, where alkyl and aryl are as defined above, are prepared.
4. The process as claimed in any of claims 1 to 3, characterized in that the oxidant used is oxygen or a gas mixture comprising at least 15 percent by volume of oxygen.
5. The process as claimed in any of claims 1 to 4, characterized in that the catalyst used is an osmium, ruthenium or manganese compound.

6. The process as claimed in any of claims 1 to 5, characterized in that the reaction proceeds at temperatures of from 20 to 200°C, preferably from 30 to 150°C, particularly preferably from 40 to 100°C, with the pressure being able to be up to 200 bar.
7. The process as claimed in any of claims 1 to 6, characterized in that the amine added to improve the selectivity is a tertiary amine, preferably a bicyclic amine of the quinuclidine type.
8. The process as claimed in any of claims 1 to 7, characterized in that the amine is introduced as a ligand.
9. The process as claimed in any of claims 1 to 8, characterized in that sulfonamides such as methylenesulfonamide and/or carboxamides are added as cocatalysts.
10. The process as claimed in any of claims 1 to 9, characterized in that the osmium compounds  $\text{OsO}_4$ ,  $\text{K}_2\text{Os}_2(\text{OH})_4$ ,  $\text{Na}_2\text{Os}_2(\text{OH})_4$ ,  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{OsCl}_3$ ,  $\text{H}_2\text{OsCl}_6$ ,  $[\text{CF}_3\text{SO}_3\text{Os}(\text{NH}_3)_5](\text{O}_3\text{SCF}_3)_2$ ,  $\text{OsO}_4$  on vinylpyridine,  $\text{Bu}^t\text{NOsO}_3$ , the manganese compounds  $\text{MnO}_2$ ,  $\text{KMnO}_4$ ,  $\text{Ca}(\text{MnO}_4)_2$ ,  $\text{MnCl}_3$ ,  $\text{Mn}(\text{OAc})_3$  and the ruthenium compounds  $\text{RuCl}_3$ ,  $\text{RuO}_4$ ,  $\text{RuO}_2$  are used as catalysts and/or catalyst precursors.
11. The process as claimed in any of claims 1 to 10, characterized in that the catalysts used are employed in amounts of from 0.2 to 0.00001 equivalents, based on olefin, preferably from 0.1 to 0.0001 equivalents and particularly preferably from 0.08 to 0.0005 equivalents.
12. The process as claimed in any of claims 1 to 11, characterized in that the ratio of amine to metal is from 0.01:1 to 1 000:1, preferably from 0.1:1 to 100:1, particularly preferably from 1:1 to 50:1.

**COMBINED DECLARATION AND POWER OF ATTORNEY**

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

**METHOD FOR THE DIHYDROXYLATION OF OLEFINS USING  
TRANSITION-METAL CATALYSTS**

the specification of which is attached hereto,

or was filed on April 18, 2000

as a PCT Application Serial No. PCT/EP00/03493

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

199 20 038.6  
(Number)

Germany  
(Country)

April 25, 1999  
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Le A 34 285-US

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